

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C03C 17/34, 17/36, C23C 14/56</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/37377</b> <b>(43) International Publication Date:</b> 29 June 2000 (29.06.00)
<b>(21) International Application Number:</b> PCT/US99/02208 <b>(22) International Filing Date:</b> 2 February 1999 (02.02.99) <b>(30) Priority Data:</b> 60/113,259 21 December 1998 (21.12.98) US <b>(71) Applicant (for all designated States except US):</b> CARDINAL IG COMPANY [US/US]; 12301 Whitewater Drive, Minnetonka, MN 55343-9447 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> KRISKO, Annette [US/US]; S-9913 Exchange Road, Prairie de Sac, WI 53578 (US). BOND, Bob [US/US]; 645 Washington, Spring Green, WI 53588 (US). STANEK, Roger [US/US]; 633 North Cincinnati, Spring Green, WI 53588 (US). PFAFF, Gary [US/US]; 1024 E. Madison Street, Spring Green, WI 53588 (US). HARTIG, Klaus [US/US]; 5871 Valley Road, Avoca, WI 53506 (US). <b>(74) Agents:</b> HOTCHKISS, Edward, S. et al.; Fredrikson & Byron, P.A., 1100 International Centre, 900 2nd Avenue South, Minneapolis, MN 55402-3397 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SOIL-RESISTANT COATING FOR GLASS SURFACES  <b>(57) Abstract</b>  A glass article which has a water-sheeting coating and a method of applying coatings to opposed sides of a substrate are described. In one embodiment, a water-sheeting coating (20) comprising silica is sputtered directly onto an exterior surface of the glass. The exterior face of this water-sheeting coating is substantially non-porous but has an irregular surface. This water-sheeting coating causes water applied to the coated surface to sheet, making the glass article easier to clean and helping the glass stay clean longer. In one method of the invention, interior and exterior surfaces of a glass sheet are cleaned. Thereafter, the interior surface of the sheet of glass is coated with a reflective coating by sputtering, in sequence, at least one dielectric layer, at least one metal layer, and at least one dielectric layer. The exterior surface of the glass is coated with a water-sheeting coating by sputtering silica directly onto the exterior surface of the sheet of glass. If so desired, both the interior surface and the exterior surface can be applied during the same pass through the same sputter coating apparatus while the glass maintains a constant orientation wherein the interior surface is positioned above the exterior surface.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**Description**

5

10

15

20

25

30

35

40

45

50

55

5

## SOIL-RESISTANT COATING FOR GLASS SURFACES

10

### FIELD OF THE INVENTION

15

5 The present invention provides a coating for glass substrates and the like which resists accumulation of dirt and water stains. Coated glass substrates of the invention can be used in insulated glass units wherein the coating of the invention is carried on an exterior surface of one pane of glass while a reflective coating is applied on the opposite side of the same pane of glass.

20

10

### BACKGROUND OF THE INVENTION

25

Keeping windows and other glass surfaces clean is a relatively expensive, time-consuming process. While cleaning any individual window is not terribly troublesome, keeping a larger number of windows clean can be a significant burden. For example, with modern glass office towers, it takes significant time and expense to have window washers regularly clean the exterior surfaces of the windows.

30

35

Windows and other glass surfaces can become "dirty" or "soiled" in a variety of ways. Two of the primary manners in which windows can collect dirt involve the action of water on the glass surface. First, the water itself can deposit or collect dirt, minerals or the like onto the surface of the glass. Obviously, dirty water landing on the glass will leave the entrained or dissolved dirt on the glass upon drying. Even if relatively clean water lands on the exterior surface of a window, each water droplet sitting on the window will tend to collect dust and other airborne particles as it dries. These particles and any other chemicals which become dissolved in the water will become more concentrated over time, leaving a characteristic spot or drying ring on the glass surface.

40

45

25

50

The second way in which water tends to give a window or other glass surface a soiled or less attractive appearance is tied to an attack on the glass surface itself. As a droplet of even relatively clean water sits on a glass surface, it will begin to leach

55

alkaline components from the glass. For a typical soda lime glass, the soda and lime will be leached out of the glass, increasing the pH of the droplet. As the pH increases, the attack on the glass surface will become more aggressive. As a result, the glass which underlies a drying water droplet will become a little bit rougher by the time the water droplet completely dries. In addition, the alkaline components which were leached out of the glass will be redeposited on the glass surface as a drying ring. This dried alkaline material not only detracts from the appearance of the glass; it will also tend to go back into solution when the glass surface is wetted again, rapidly increasing the pH of the next water droplet to coalesce on the glass surface.

In storing and shipping plate glass, the presence of water on the surfaces between adjacent glass sheets is a chronic problem. One can take steps to shield the glass from direct contact with water. However, if the glass is stored in a humid environment, water can condense on the glass surface from the atmosphere.

This becomes more problematic when larger stacks of glass are collected. Large stacks of glass have a fairly large thermal mass and will take a long time to warm up. As a consequence, they will often be cooler than the ambient air when ambient temperature increases (e.g., in the morning), causing moisture in the air to condense on the surface of the glass. Due to limited air circulation, any moisture which does condense between the sheets of glass will take quite a while to dry. This gives the condensed moisture a chance to leach the alkaline components out of the glass and adversely affect the glass surface. The rate of attack can be slowed down somewhat by applying an acid to the surface of the glass. This is commonly done by including a mild acid, e.g., adipic acid, in the separating agent used to keep glass sheets from sticking to and scratching one another.

A number of attempts have been made to enable a glass sheet to keep a clean appearance longer. One avenue of current investigation is a "self-cleaning" surface for glass and other ceramics. Research in this area is founded on the ability of certain metal oxides to absorb ultraviolet light and photocatalytically break down biological materials such as oil, plant matter, fats and greases, etc. The most powerful of these photocatalytic metal oxides appears to be titanium dioxide, though other metal oxides

5 which appear to have this photocatalytic effect include oxides of iron, silver, copper, tungsten, aluminum, zinc, strontium, palladium, gold, platinum, nickel and cobalt.

10 While such photocatalytic coatings may have some benefit in removing materials of biological origin, their direct impact on other materials is unclear and appears to vary with exposure to ultraviolet light. As a consequence, the above-noted  
15 problems associated with water on the surface of such coated glasses would not be directly addressed by such photocatalytic coatings.

A number of attempts have been made to minimize the effect of water on glass surfaces by causing the water to bead into small droplets. For example, U.S. Patent  
20 5,424,130 (Nakanishi, et al., the teachings of which are incorporated herein by reference) suggests coating a glass surface with a silica-based coating which incorporates fluoroalkyl groups. The reference teaches applying a silicone alkoxide  
25 paint onto the surface of the glass, drying the paint and then burning the dried paint in air. Nakanishi, et al. stress the importance of substituting part of the non-metallic atoms, i.e., oxygen in a layer of SiO<sub>2</sub>, with a fluoroalkyl group. Up to 1.5% of the  
30 oxygen atoms should be so substituted. Nakanishi, et al. state that if less than 0.1% of the oxygen atoms are substituted with a fluoroalkyl group, the glass won't repel water properly because the contact angle of water on the glass surface will be less than 80°.

35 20 Such "water repellent" coatings do tend to cause water on the surface of the glass to bead up. If the coating is applied to an automobile windshield or the like where a constant flow of high velocity air is blowing over the surface, this water  
40 beading effect can help remove water from the glass surface by allowing the droplets to blow off the surface. However, in more quiescent applications, these droplets will  
25 tend to sit on the surface of the glass and slowly evaporate. As a consequence, this supposed "water repellent" coating will not solve the water-related staining problems noted above. To the contrary, by causing the water to bead up more readily, it may  
45 actually exacerbate the problem.

50 30 Other silica coatings have been applied to the surface of glass in various fashions. For example, U.S. Patent 5,394,269 (Takamatsu, et al.) proposes a "minutely rough" silica layer on the surface of glass to reduce reflection. This

roughened surface is achieved by treating the surface with a supersaturated silica solution in hydrosilicofluoric acid to apply a porous layer of silica on the glass sheet. By using a multi-component of sol gel solution, they claim to achieve a surface which has small pits interspersed with small "islet-like land regions" which are said to range from about 50-200 nm in size. While this roughened surface may help reduce reflection at the air/glass interface, it appears unlikely to reduce the water-related staining problems discussed above. If anything, the porous nature of this coating appears more likely to retain water on the surface of the glass. In so doing, it seems probable that the problems associated with the long-term residence of water on the glass surface would be increased.

#### SUMMARY OF THE INVENTION

In one aspect, the present invention provides a glass article which has a water-sheeting coating and a method of applying such a coating. In accordance with a first embodiment of this invention, a glass article has at least one coated surface bearing a water-sheeting coating. This water-sheeting coating comprises silica sputtered directly onto an exterior surface of the glass. The water-sheeting coating has an exterior face which is substantially non-porous, but which has an irregular surface. This water-sheeting coating desirably reduces the wetting angle of water on the coated surface of the glass article below about 25° and causes water applied to the coated surface of the glass article to sheet.

In accordance with a second embodiment of the invention, a window is provided having at least one pane of glass having an exterior surface exposed to periodic contact with water. The exterior surface of this pane of glass has a water-sheeting coating comprising silica sputtered directly on the glass surface to a mean thickness of between about 15 Å and about 350 Å. This water-sheeting coating has an exterior face which is substantially non-porous, but which has an irregular surface. The water-sheeting coating causes water applied to the coated surface of the pane of glass to sheet.

5  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55

In a further embodiment of the invention, a sheet of glass has an interior surface bearing a reflective coating thereon and an exterior surface bearing a water-sheeting coating thereon. The reflective coating may comprise a reflective metal layer and at least one dielectric layer. The water-sheeting coating again comprises silica sputtered directly onto the exterior surface of the sheet of glass and this water-sheeting coating has an exterior face which is substantially non-porous, but which has an irregular surface. This water-sheeting coating desirably reduces the contact angle of water on the coated surface of the sheet of glass below about 25° and causes water applied to the coated exterior surface of the pane to sheet.

10  
15  
20  
25  
30  
35  
40  
45  
50  
55

As noted above, the present invention also contemplates a method of rendering a glass surface resistant to soiling and staining. In one embodiment, the method comprises first providing a sheet of glass having an interior surface and an exterior surface. The interior and exterior surfaces of the glass are cleaned. Thereafter, the interior surface of the sheet of glass is coated with a reflective coating by sputtering, in sequence, at least one first dielectric layer, at least one metal layer, and at least one second dielectric layer. The exterior surface of the glass is coated with a water-sheeting coating by sputtering silica directly onto the exterior surface of the sheet of glass. If so desired, the water-sheeting coating can be applied on the same sputter coating apparatus used to create the reflective coating. With appropriate material selection, the water-sheeting coating and one of the dielectric layers of the reflective coating may even be applied in the same sputtering chamber in an oxidizing atmosphere. If so desired, the pane of glass can be coated on both the interior surface and the exterior surface while maintaining the glass in a constant orientation wherein the interior surface is positioned above the exterior surface.

25  
30  
35  
40  
45  
50  
55

In accordance with an alternative method of the invention, a sheet of glass having an interior surface and an exterior surface is provided. A sputtering line is also provided, the sputtering line comprising a series of sputtering chambers, each having a support for a sheet of glass therein. At least one of the sputtering chambers comprises a dual direction sputtering chamber having an upper target position above the support and a lower target position below the support. The interior and exterior surface of the glass are cleaned and, thereafter, the sheet of glass is positioned on the



support in the dual direction supporting chamber such that the interior surface is oriented toward the upper target and the exterior surface is oriented toward the lower target. The upper target is sputtered to deposit a dielectric layer. This dielectric layer may be deposited directly on the interior surface of the glass or on a film stack layer previously deposited on the interior surface of the glass. While the sheet of glass remains in the dual direction sputtering chamber, the lower target is sputtered to deposit a water-sheeting coating on the exterior surface of the glass. In one possible preferred embodiment, both the upper target and the lower target are sputtered in an oxidizing atmosphere within the same sputtering chamber.

In yet another embodiment, the invention provides a method of coating two sides of a single pane of glass or other substrate in a single pass through a coating apparatus, regardless of the nature of the coating being applied to either side of the glass. In this method, a sheet of glass (or other substrate) having a clean interior surface and a clean exterior surface is provided. A sputtering line is also provided, this line comprising a series of sputtering chambers each having a support for a sheet of glass therein, at least one of the sputtering chambers comprising a downward sputtering chamber having an upper target positioned above the support. A second of the sputtering chambers comprises an upward sputtering chamber having a lower target positioned below the support. The sheet of glass or other substrate is positioned on the support in the downward sputtering chamber such that the interior surface is oriented toward the upper target. The upper target is sputtered to deposit a coating directly on one of the interior surface of the glass or a film stack layer previously deposited on the interior surface of the glass. The sheet of glass is also positioned on the support in the upward sputtering chamber such that the exterior surface is oriented toward the lower target. The lower target is sputtered to deposit a coating on one of the exterior surface of the glass or a film stack layer previously deposited on the exterior surface of the glass. The glass is coated on both the interior surface and the exterior surface while maintaining a constant orientation wherein the interior surface is positioned above the exterior surface.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic cross-sectional view of a sheet of glass bearing a coating in accordance with the invention;

Figure 2 is a schematic cross-sectional illustration of a multi-pane insulated glass unit incorporating a water-sheeting coating of the invention;

Figure 3 is a schematic cross-sectional view of a laminated window structure of the type commonly used in automobile windshields bearing a water-sheeting coating of the invention;

Figure 4 is a schematic illustration of a dual direction sputtering chamber for use in accordance with the invention;

Figure 5 is a schematic illustration of a multiple-zone dual direction sputtering chamber for use in accordance with another embodiment of the invention;

Figure 6 is an atomic force micrograph of a plain, uncoated surface of a sheet of conventional float glass;

Figure 7 is a graph showing a height profile across a short length of the surface of the sheet of glass shown in Figure 6;

Figure 8 is a atomic force micrograph of a surface of a sheet of float glass bearing a water-sheeting coating in accordance with the invention;

Figure 9 is a three-dimensional representation of an area of the same sheet of float glass illustrated in Figure 8; and

Figure 10 is a graph similar to Figure 7, but showing a height profile across a short length of the surface of the water-sheeting coating shown in Figures 8 and 9.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Figure 1 schematically illustrates a sheet of glass bearing a pair of coatings in accordance with one useful embodiment of the invention. The sheet of glass 10 includes an exterior face 12 and an interior face 14. (The designation of "interior" and "exterior" face in the ensuing discussion is somewhat arbitrary. It is assumed, though,

5 that in most circumstances the exterior face will be exposed to an ambient  
environment wherein it may come into contact with dirt, water and the like. The interior  
10 face may also be oriented toward the same kind of ambient environment. In the  
embodiments illustrated in Figures 2 and 3, though, this "interior" face is actually  
5 protected and a second pane of glass stands between this interior face and the  
ambient environment.)

15 The interior face 14 of the glass 10 bears a reflective coating 30. As those  
skilled in the art will readily recognize, this reflective coating may take any desired  
form depending on the desired properties. A wide variety of such films are known in  
20 the art and the precise nature of the reflective coating 30 is beyond the scope of the  
present invention.

25 If, for example, the glass article is to be used as a mirror, the coating 30 may  
simply comprise a relative thick layer of a reflective metal. If so desired, a protective  
coating of a dielectric material may be applied over the surface of the metal opposite  
15 the surfacing contact with the glass. As is known in the art, this will help protect the  
metal layer from chemical and physical attack. One could also employ any of a variety  
30 of mirror coatings known in the art which comprise a layer of a dielectric on either side  
of a reflective metal layer; many dichroic mirrors known in the art employ such a

35 In the embodiment of Figure 1, the reflective coating 30 is typified as an infrared  
20 reflective coating of the type commonly used in low emissivity solar control films.  
Typically, such films will comprise a metal layer sandwiched between a pair of  
dielectric layers. This structure may be repeated to further enhance the infra-reflective  
40 properties of the film stack. One example of a useful infrared reflective film stack is  
disclosed in U.S. Patent 5,302,449 (Eby, et al.), the teachings of which are  
25 incorporated herein by reference.

45 The illustrative film stack 30 of Figure 1 includes a base coat 32 which may  
comprise one or more layers of dielectric materials. For example, this base coat 32  
may comprise zinc oxide applied at a thickness of about 150-275 Å. A first metal layer  
34 may be applied directly on top of this base coat 32. This metal may be, for  
50 30 example, silver applied at a thickness of between about 100 Å and about 150 Å. A  
second dielectric layer 38 may be applied over the first metal layer 34. The thickness

of this dielectric layer 38 will depend, at least in part, on whether a second metal layer 40 will be included in the film stack. In a film stack having two metal layers, as shown, this second dielectric layer 38 may typically comprise a relatively thick layer of a metal oxide, such as 700-750 Å of zinc oxide. If so desired, a relatively thin sacrificial layer 36 may be applied between the metal layer 34 and the dielectric layer 38. This will help protect the metal layer 34 during the sputter deposition of the dielectric layer 38. The sacrificial layer 36 may, for example, comprise a layer of titanium metal applied at a thickness of 25 Å or less. This titanium metal will oxidize sacrificially during the application of a metal oxide dielectric 38, limiting any damage to underlying silver layer 34.

In the illustrated film stack, a second metal layer 40 is applied over the second dielectric layer 38. The second metal layer 40 will usually be made of the same material as is the first metal layer 34. For example, this second metal layer 40 may comprise about 125-175 Å of silver. Again, a sacrificial layer 42 of titanium or the like may be applied over the metal layer 40 to protect the metal layer during subsequent deposition of the overlying dielectrics 44 and 46. A third dielectric layer 44 is applied over the sacrificial layer 42. This dielectric layer 44 can also be a metal oxide, e.g., zinc oxide applied at about 250-300 Å. If so desired, a protective overcoat 46 of another dielectric material can be applied over the dielectric layer 44. In one preferred embodiment, this overcoat 46 may comprise a 50-60 Å layer of  $\text{Si}_3\text{N}_4$ .

The water-sheeting coating 20 was applied to the inner surface 12 of the glass. It is preferred that this coating be applied directly on the surface of the glass sheet 12. As the glass, which will typically be a soda/lime glass, is largely formed of silica and the water-sheeting coating is also desirably formed of silica, this is believed to provide a strong bond between these two layers and may enhance the water-sheeting performance of the coating 20.

The water-sheeting coating 20 of the invention desirably comprises silica deposited directly on the exterior surface 12 of the glass 10. As will be discussed below in connection with Figures 8-10, the exterior face 22 of this coating 20 has an irregular surface. (This is schematically shown as a series of irregularly-spaced and -sized spikes on the exterior face 22 of the coating 31). Accordingly, attributing any

specific thickness to this coating 20 will be inherently somewhat inaccurate. However, the coating 20 desirably has a median thickness of between about 15 Å and about 350 Å, with a range of between about 15 Å and about 150 Å being preferred. The major benefit of this coating at the least cost is believed to be evidenced at a range of about 20 Å to about 120 Å. One preferred manner in which this coating 20 may be applied to the exterior surface 12 of the glass 10 will be discussed in more detail below.

Figure 2 is a schematic illustration of a multi-pane insulated glass unit in accordance with a further embodiment of the invention. Insulated glass units are well known in the art and may not be discussed in any significant detail here. Briefly, though, such an insulated glass unit would generally comprise two panes of glass 10, 100 held in a spaced-apart relationship by a spacer 110. In this embodiment, the water-sheeting coating 20 carried by the exterior surface of the glass 10 is oriented away from the second pane of glass 100 while the reflective coating 30 carried by the interior face of the glass 10 is oriented toward the second pane of glass 100. The spacer 110 is bonded on one side to the interior surface 102 of the second glass pane 100 and on the other side to the first glass pane 10. As is known in the art, the spacer may be bonded directly to the interior surface 14 of the glass 10 or the reflective coating 30 may extend out to the margins of the glass 10 and the spacer may be attached directly to that coating 30.

Typically, the spacer will be formed of metal or the like and will have a desiccant 112 retained therein. This desiccant will be allowed to communicate with the gas in the interpane space 115 to remove any moisture which may seep between the panes of glass. An exterior seal 114 may be carried around the external periphery of the spacer 110 to form a reliable gas and moisture barrier.

Figure 3 illustrates another application for a coated glass article of the invention. In this embodiment, the glass sheet 10 is bonded to a second sheet of glass 100 by an intermediate tear-resistant plastic film 130 to form a laminated structure. Such laminated window structures are well known in the field of automobile windows. Typically, this plastic layer 130 will take the form of a relatively thick layer of polyvinylbutyral or the like which is heat-fused to the other two sheets of glass. If so desired, the coating 30 may be omitted. More preferably, though, the reflective film 30

5 will comprise a heat-temperable infrared reflective film. A variety of such films are known in the art and the precise nature of this film is beyond the scope of the present invention, but any suitable heat-temperable coating 30 may be used.

10 As noted above, the water-sheeting coating is desirably applied by sputtering, as is the reflective coating 30, if present. These separate coatings can be applied using conventional sputtering equipment by applying the two coatings in separate passes through a sputtering line. For example, before the reflective coating is applied, the water-sheeting coating 20 of the invention can be applied to the exterior surface of the glass by positioning this surface of the glass beneath a silicon target in an oxidizing sputtering atmosphere. Thereafter, a multiple-layer reflective coating can be applied using a series of sputtering chambers in a conventional manner, with each chamber being adapted to sputter one or more specific layers of the desired film stack.

25 Figure 4 schematically illustrates a dual direction sputtering chamber in accordance with one embodiment of the present invention. Magnetron sputtering chambers are well known in the art and are commercially available from a variety of sources. While a thorough discussion of such magnetron sputtering chambers is beyond the scope of the present disclosure, one relatively useful structure for such a device is disclosed in U.S. Patent 5,645,699 (Sieck), the teachings of which are incorporated herein by reference.

35 20 Generally speaking, though, magnetron sputtering involves providing a target formed of a metal or dielectric which is to be deposited on the substrate. This target is provided with a negative charge and a relatively positively charged anode is positioned adjacent the target. By introducing a relatively small amount of a desired gas into the chamber adjacent the target, a plasma of that gas can be established. Atoms in this plasma will collide with the target, knocking the target material off of the target and sputtering it onto the substrate to be coated. It is also known in the art to include a magnet behind the target to help shape the plasma and focus the plasma in an area adjacent the surface of the target.

50 30 In Figure 4, the sheet of glass 10 to be coated is positioned on a plurality of support rollers 210 which are spaced along the length of the sputtering chamber 200. While the precise spacing of these rollers 210 can be varied, for reasons explained

more fully below, it is desired that these rollers are spaced a little bit farther apart along at least a interim length of the chamber 200 to increase the effective coating area from the lower target 260.

In the illustrated embodiment, the sheet of glass 10 is oriented to travel horizontally across these rollers, e.g., from left to right. The interior surface 14 of the glass is oriented upwardly while the exterior surface 12 of the glass is oriented downwardly to rest on the rollers 210. (While this is probably the most typical configuration, it should be understood that the relative orientation of the glass within the sputtering chamber 200 can be switched so long as the relative positions of the upper targets 200 and the lower target 260 are also reversed. As a consequence, it should be noted that designating these targets as "upper" and "lower" targets is simply for purposes of convenience and the relative orientation of these elements within the sputtering chamber can easily be reversed if so desired.)

The sputtering chamber 200 shown in Figure 4 includes two spaced-apart upper sputtering targets 220a and 220b. While these targets can be planar targets, they are illustrated as being so-called rotary or cylindrical targets. These targets are arranged generally parallel to one another with a plurality of anodes 230 extending horizontally and generally parallel to these targets. As suggested in U.S. Patent 5,645,699, an intermediate anode 230 may also be positioned between these two targets.

A gas distribution system is used to supply the sputtering gas to the chamber adjacent the targets 220a and 220b. While a variety of gas distribution systems are known in the art, this distribution system may simply comprise a pair of pipes 235 with a plurality of spaced-apart openings or nozzles oriented generally toward the target.

The use of multiple targets positioned above a glass substrate in a magnetron sputtering chamber is fairly conventional in the field. The unique aspect of the sputtering chamber 200 Figure 4, though, is the presence of the "lower" target 260. This target is the target used to sputter the water-sheeting coating 20 of the invention directly on the exterior surface 12 of the glass. As with the upper targets 220a and 220b, the lower target 260 is provided with at least one, and preferably two, anodes 270 in sufficient proximity to establish a stable plasma. The gas distribution pipes 235

5 shown adjacent the upper targets 220a and 220b are undesirably far from the lower  
target 260 and the intermittent presence of the glass 10 will effectively divide the  
10 sputtering chamber 200 into two separate functional areas. Accordingly, it is preferred  
to have separate gas distribution pipes 275 positioned beneath the gas adjacent the  
15 lower target 260 to ensure a consistent supply of gas for the plasma adjacent the  
target. If so desired, the lower pipes 275 and the upper pipes 235 may be a part of the  
same gas distribution system, i.e., both sets of pipes can be connected to a single gas  
supply.

20 The nature of the gas supplied by the lower pipes 275 will depend at least in  
part on the nature of the sputtering target 260. In conventional magnetron sputtering,  
the target must serve as a cathode. Due to the dielectric nature of  $\text{SiO}_2$ , it can be  
25 exceedingly difficult to reliably sputter using a silica target. As a consequence, it is  
preferred that the target comprise silicon metal rather than silica. The material actually  
deposited on the exterior surface 12 of the glass can be converted to silica by  
30 including oxygen in the gas supplied through the lower gas distribution pipes 275.

35 While the successive sheets of glass 10 will effectively divide the sputtering  
chamber, this does not preclude gas introduced in one area of the chamber from  
travelling elsewhere in the chamber. As it is preferred that the lower target 260  
comprise silicon metal sputtered in an oxidizing atmosphere, it is important that the  
40 sputtering of the upper targets 220a and 220b not be adversely affected by the  
presence of any excess oxygen which may be introduced through the lower pipes 275.  
This may effectively preclude the use of this dual direction sputtering chamber 200 to  
45 deposit a water-sheeting coating 20 on one side of the glass sheet and an oxygen-  
sensitive metal on the other surface.

50 25 More advantageously, the dual direction sputtering chamber of Figure 4 can be  
used to deposit a dielectric layer on the interior surface 14 of the glass and the silica



- 14 -

5 water-sheeting coating 20 on the exterior surface 12 of the glass in a single chamber.

10 The sputtered dielectric may be a nitride or the like so long as the introduction of some metal oxide into the nitride being deposited will not adversely affect the coating being applied. Ideally, though, the dielectric being applied to the interior surface 14 is an

15 oxide (or at least a partial oxide) so that any commingling of the gases introduced through the two sets of pipes 235 and 275 will not adversely affect either the dielectric layer or the water-sheeting coating. For example, one or both of the targets 220a and

20 220b may be made of titanium metal or  $\text{TiO}_x$  (where  $1 < x < 2$ ) and the gas introduced through both sets of gas distribution pipes 235 and 275 may comprise an appropriately

25 balanced mixture of argon and oxygen.

30 In conventional magnetron sputtering chambers, the spacing of the rollers 210 used to support the glass is kept fairly small to permit smaller glass substrates to be processed on the line without any significant risk of having the glass fall between the rollers. In order to minimize the interference of the rollers in applying the water-

35 sheeting coating on the exterior surface 12 of the glass, though, this spacing may be increased. The maximum safe spacing will need to be determined on a case-by-case basis for a given range of anticipated glass sizes. However, the larger the spacing

40 between the rollers disposed in the path from the lower target 260 to the exterior surface 12 of the glass, the greater the percentage of the sputtered silica which will be

45 deposited on the glass. Of course, the rollers in other areas of the sputtering apparatus can be maintained at their normal spacing. It may be desirable to make a few of the rollers in the dual direction sputtering chamber 200 easily removed so the

50 chamber can be converted from the illustrated configuration to a more conventionally

55

5 operated chamber coating only one side of the glass and having rollers spaced more closely together.

10 Instead of changing the spacing between the rollers, the rollers could instead be made smaller in diameter. Conventional rollers are hollow metal tubes. If so  
15 desired, the smaller diameter rollers can be stiffened, e.g., by filling them with a rigid foam. In order to maintain the same transport speed of the glass along the support, these smaller-diameter rollers would have to be turned more rapidly, e.g., by means of  
20 a pair of gears having the desired gear ratio.

The rollers 210 can be of any conventional structure. It has been found that  
10 good results can be obtained by employing cylindrical aluminum rollers about which a rope of Kevlar™ is spirally wound, with the Kevlar™ providing the surface with which  
25 the glass is in direct contact.

30 In some specific applications, the dual direction sputtering chamber 200 of Figure 4 may be sufficient to apply the entire desired coating to both the interior and  
15 exterior surfaces of the glass. More often, though, the sputtering chamber 200 would be part of a sputtering line comprising a series of sputtering chambers. Each  
35 sputtering chamber in the line could include both an upper target and a lower target, but in most conventional applications the film stack applied to the upper surface of the  
40 glass will be more complex (i.e. will comprise a series of distinct layers of varying composition) and thicker than is the water-sheeting coating of the invention. As a  
20 consequence, a majority of the sputtering chambers can comprise conventional, downward sputtering chambers having only an upper target, with no target positioned  
45 beneath the supports.  
50

5 If the sputtering line comprises a combination of downward sputtering chambers  
and dual direction sputtering chambers 200, the position of the dual direction  
10 chambers along the sputtering line can be varied. If the water-sheeting coating of the  
invention is applied by sputtering a silicon-containing target (e.g., one formed primarily  
15 of silicon or formed of silicon doped with aluminum) in an oxidizing atmosphere, one  
should not attempt to deposit an oxidizable metal layer (e.g., an infrared reflective  
silver layer of the type conventionally used in low emissivity film stacks) on the upper  
20 surface of the glass in the same chamber. Accordingly, at least those chambers used  
to sputter a metal layer may be operated as a downward sputtering chamber by  
10 omitting the lower target. It would be possible, though, to deposit a metal oxide (e.g.,  
25  $\text{SiO}_2$ ,  $\text{ZnO}$  or  $\text{SnO}_2$ ) on the upper surface of the glass in the same chamber.

Conventional wisdom would suggest to one skilled in the art that the water-  
30 sheeting coating of the invention be applied in the first sputtering chamber or, if  
necessary, the first several sputtering chambers to make sure that the water-sheeting  
15 coating is applied before the glass surface is damaged or soiled by contact with the  
35 rollers supporting the glass within the chambers. Quite surprisingly, it has been found  
that the opposite is true - the water-sheeting coating of the invention is optimally  
40 applied in the last sputtering chamber. If more than one dual direction sputtering  
chamber 200 is necessary to deposit a sufficiently thick water-sheeting coating without  
20 unduly slowing down glass speed through the sputtering line, the water-sheeting  
45 coating is optimally applied in the last few sputtering chambers.

If the water-sheeting coating of the invention is applied at the beginning of the  
50 sputtering line, the majority of the exterior surface of the glass will exhibit the desired  
water-sheeting properties. However, the margins of the glass may not exhibit these

- 17 -

5 improved properties on a consistent basis. This is believed to be due to a slight  
overspray of the coating applied to the upper surface of the glass after deposition of  
10 the water-sheeting coating, wherein a very small amount of the material being applied  
to the upper surface will drift down to the lower surface and overlie the water-sheeting  
15 coating adjacent the edges of the glass sheet. While this oversprayed coating is thin  
enough as to have no readily discernable effect on the optical properties of the glass,  
this virtually invisible coating compromised the benefits of the water-sheeting coating  
20 around the edges of the glass. By applying the silica to the exterior surface of the  
glass toward the end of the sputtering line, the amount of overspray deposited on top  
10 of the silica coating can be minimized and the beneficial water-sheeting effects of this  
25 coating can be preserved.

A dual direction sputtering chamber 200 such as that shown in Figure 4 is  
30 believed to minimize the cost and maximize production efficiency in applying coatings  
to both sides of the sheet of glass. Less desirably, a water-sheeting coating of the  
15 invention could be applied in one pass while the reflective coating is applied to the  
35 other side of the glass in a second pass, flipping the glass between the passes to  
permit all of the targets to be positioned on the same side of the supports in the  
chamber(s). This is much less efficient than the process outlined above, though, and  
40 is not believed to be suitable for low-cost commercial glass production.

20 As the glass substrate moves through the chamber, there will be times when  
45 the glass does not effectively shield the upper targets 200a and 200b from the lower  
target 260 or vice versa. As a consequence, material from the upper targets will be  
deposited on the lower target and material from the lower target can be deposited on  
50 one or both of the upper targets. The sputtering chamber 200 of Figure 4 is ideal if the

55

upper targets 220a, 220b and the lower target 260 have substantially the same composition. If the upper targets have a different composition from the lower target, though, the cross-contamination of the different targets can lead to problems in sputtering or in maintaining consistent product quality.

At least in theory, this problem may be overcome by independently controlling the power supplied to each of the sputtering targets to ensure that each target is sputtering only when the glass is positioned to shield the upper and lower targets from one another. Current commercially available power supply controllers are not configured in this fashion, however. Furthermore, the control logic for such an arrangement can be unduly difficult if the sputtering line is used to coat glass substrates of varying sizes rather than a consistent size.

Figure 5 illustrates one possible sputtering chamber 300 which can be used to coat both the interior surface 14 and the exterior surface 12 of the substrate in a single pass without significant cross contamination of the sputtering targets. Elements serving an analogous function to elements shown in Figure 4 bear like reference numbers, but indexed by 100, e.g., the upper gas distribution pipes 335 of Figure 5 are functionally analogous to the upper gas distribution pipes 235 of Figure 4.

The sputtering chamber 300 of Figure 5 is effectively divided into three coating zones 300a, 300b and 300c by a pair of barriers 340. Some fraction of the gas in one coating zone may flow into another coating zone, so it is best to use a similar atmosphere in all three zones. However, the barriers 340 serve to effectively limit the amount of material sputtered in one coating zone which lands on a target in another coating zone.

5 In the embodiment of Figure 5, each of the three coating zones 300a-300c is adapted to hold up to four targets, with two targets positioned above the substrate and  
10 two positioned below the substrate. Hence, there are six upper target mounts 321-326 positioned above the path of the glass and six lower target mounts 361-366 positioned  
15 beneath the path of the glass. This allows maximum flexibility in using this single multi-zone sputtering chamber 300 to manufacture products having different properties. Figure 5 schematically illustrates each of the upper target mounts 321-326  
20 vertically aligned with one of the lower target mounts 361-366, respectively. It should be understood, however, that the targets need not be vertically aligned in this fashion  
10 and may be more advantageously positioned in a horizontally staggered arrangement.

25 In the configuration shown in Figure 5, the first coating zone 300a has two upper targets (320a and 320b), but no lower targets on the lower target mounts 361 or  
30 362. While a sputtering gas should be supplied to the upper gas distribution pipes 335 and power should be supplied to the upper anodes 330 in the first coating zone, there  
15 is no need to deliver any gas to the lower gas distribution pipes 375 or any power to the lower anodes 370. The second coating zone 300b has two lower targets 360c and  
35 360d, but neither of the upper target mounts 323 and 324 carry sputtering targets. Similarly, the third coating zone 300c has two lower targets 360e and 360f, but neither  
40 of the upper target mounts 325 and 326 carry sputtering targets. Optimally (as  
20 discussed above), the first coating zone 300a is used to apply the outermost layer of the reflective film stack carried by the interior surface 14 of the substrates while the  
45 last two coating zones 300b and 300c are used to sputter the water-sheeting coating 20 on the exterior surface 12 of the substrates.

- 20 -

5 The arrangement of targets in the multiple-zone sputtering chamber 300 of  
Figure 5 is merely illustrative and it should be understood that the target arrangement  
10 can be varied to maximize production efficiency for different products. For example, if  
a thicker water-sheeting coating is desired at the same glass speed, a silicon-  
15 containing target can be mounted on each of the lower target mounts 361-366 while  
none of the upper target mounts 321-326 carry a target. If a thinner coating will suffice  
(or if glass speed through the coating chamber is suitably reduced), only the last two  
20 lower target mounts 325 and 326 can be provided with targets while each of the first  
four upper target mounts 321-324 carry sputtering targets. Of course, any one or  
25 more of the coating zones 300a-300c can be operated much like the dual-direction  
sputtering chamber 200 of Figure 4 by mounting targets in the upper and lower target  
mounts of the same zone.

30 The apparatus of Figures 4 and 5 and the method of depositing coatings using  
such coating systems is discussed in the present application primarily in the context of  
15 applying a reflective film stack on one side of the glass and a water-sheeting coating  
35 on the other side of the glass. It is to be understood, however, that this apparatus and  
method can be used to apply coatings to both sides of a pane of glass regardless of  
40 the nature of the coatings applied thereto. For example, the apparatus can be used to  
apply an anti-reflective coating on both sides of a pane of glass, to apply infrared  
20 reflective coatings to both sides of a transparent or translucent organic substrate, or to  
45 apply a water-sheeting coating to each side of the same substrate.

The advantage of the systems illustrated in Figures 4 and 5 is that a substrate  
50 can be provided with a sputtered coating (regardless of composition) on both sides in  
a single pass through the coating apparatus while the glass is maintained in a

55

5 constant orientation, i.e. wherein it does not need to be flipped, turned or otherwise  
manipulated. This enables the use of a simple set of standard transport rollers to  
10 move the glass along the production line. In the absence of the present invention, one  
typically would have to either manually handle the glass to flip it and send it back  
15 through the coating apparatus in a separate run, or use a complex glass handling  
system which must hold the substrate and flip it at some point during the production  
process. This enables glass having coatings on both sides to be produced  
20 particularly economically without any loss in coating quality.

In the past, it was assumed that even if one were to coat the bottom side of the  
10 glass, contact with the rollers would mar that coating or and/or damage the bottom  
25 surface of the glass prior to application of the coating. Surprisingly, however, the  
present invention demonstrates that both sides of the glass can be coated in a single  
30 pass with excellent results.

The precise operating conditions (e.g. target composition, plasma composition,  
15 etc.) under which the water-sheeting coating of the invention is applied can be varied  
35 as necessary to optimize the deposition of a coating of the desired thickness. Given  
the present teaching as a guide, one of ordinary skill in the art should be able to select  
40 suitable operating conditions to apply a coating of the invention without undue  
experimentation.

20 A layer of  $\text{SiO}_2$  in accordance with the invention may be sputter deposited using  
45 a silicon dioxide target in an inert atmosphere, but silica is a poor conductor and it can  
be difficult to sputter such dielectric materials in a DC sputtering apparatus. One could  
instead use a pure silicon target in an oxidizing atmosphere, but such targets are  
50 difficult to sputter in a consistent, controlled fashion because silicon is a



semiconductor. To improve sputtering and reduce arcing, it is preferred that a target comprising silicon with about 5% aluminum be sputtered in an oxidizing atmosphere.

Even if an aluminum-doped silicon target is employed, the atmosphere in the sputtering chamber can be varied to achieve the optimum sputtering rate. While the sputtering atmosphere should be oxidizing, it need not be pure oxygen. To the contrary, a mixture of oxygen and an inert gas will enhance the sputtering rate. It is believed that a sputtering gas comprising oxygen and up to about 40% argon (preferably 0-20% argon) maintained at about  $3 \times 10^{-3}$  mbar will suffice. The power applied to the sputtering target should be optimized to reduce arcing yet maximize sputtering rate. A power of up to about 80 kW should yield acceptable results.

One manufacturing arrangement which has been found to work well utilizes three rotary sputtering targets of silicon doped with about 5% aluminum, with a power of about 42 kW being applied to each target. The atmosphere in the sputtering chamber comprises 100% O<sub>2</sub> at a pressure of about 2.5-4.5 mTorr. The glass substrate is moved past these sputtering targets at about 225-500 inches per minute.

In manufacturing float glass, molten glass is floated on a bath of molten tin and the glass is referred to as having an upper side and a lower, or "tin" side. Most commonly, when float glass is provided with a reflective coating, the coating is applied to the upper side of the glass due to some minor surface imperfections in the tin side of the glass which can arise due to contact with support rollers in the annealing lehr. If a sheet of float glass 10 is to be provided with both a water-sheeting coating 20 and a reflective layer 30, it is preferred that the upper surface of the sheet glass be used as the interior surface 14 of the glass to receive the reflective coating 30 while the tin side of the glass is used as the exterior surface to receive the water-sheeting coating 20.

Figure 6 is an atomic force micrograph of one square micron ( $\mu\text{m}$ ) of the surface of the tin side of an untreated sheet of float glass. Figure 7 is a graph

5 representing a profile of the same side of the sheet of glass along about a 1  $\mu\text{m}$  line on  
that surface. Both of these images were obtained by atomic force microscopy using a  
10 Digital Instruments Nanoscope III using a standard silicon tip.

15 Figures 6 and 7 illustrate a relatively smooth surface. While this surface is not  
perfectly smooth and it appears to have a slightly rough appearance in Figure 6, it is  
important to note that the scale of these images is quite small. To place these images  
in perspective, two peaks in the profile of Figure 7 are highlighted by a pair of arrows.  
The two darker arrows toward the left in Figure 7 (at about 0.25  $\mu\text{m}$  along the  
20 abscissa) mark the beginning and the apex of a first peak A; the two lighter arrows  
toward the right in Figure 7 (at about 0.9  $\mu\text{m}$  along the abscissa) mark the apex and  
end of a second peak B. The first peak A is less than 0.7 nm in height while the  
second, taller peak B is only about 1.7 nm tall.

25 Figures 8-10 are analogous representations of a sheet of float glass on the tin  
side of which a water-sheeting coating of the invention has been applied. Figure 8 is a  
15 micrograph much like Figure 6, also representing 1  $\mu\text{m}^2$  of the surface. Figure 10 is a  
graph much like Figure 7, but wherein the ordinate axis represents a range of 20 nm  
rather than the smaller 5nm range of Figure 7. Figure 9 is a perspective view which  
30 highlights the surface features of the water-sheeting coating. The smaller vertical bar  
to the right of the primary image is a legend representing the gray scale associated  
with different heights from the base surface.

35 By comparing these two sets of figures, it appears that the water-sheeting  
coating of the invention has a significantly more irregular surface than does the  
uncoated surface shown in Figures 6 and 7. In Figure 8, there appear to be a series  
40 of spaced-apart projections rising from the surface of the glass, but it is difficult to  
determine in this view the height of these projections. Figures 9 and 10 give a better  
25 indication of the height and shapes of these projections. In Figure 10, the two darker  
arrows highlight the apex and end of one peak A while the two lighter arrows point to  
the apex and end of a second peak B. In contrast to the rather small peaks in Figure  
45 7, the second, smaller peak B in Figure 10 is about 4.3 nm tall while the first peak A is  
nearly 10 nm tall. This is over five times as tall as the peaks illustrated in Figure 7.

5 It is also worth noting that the surface of the coating shown in Figures 8-10 is  
10 uneven, but appears to be relatively non-porous. This is in sharp contrast to the  
photomicrographs in Takamatsu et al.'s US Patent 5,394,269, which show a porous  
sol gel-derived coating having pores on the order of 50-200 nm penetrating the  
15 coating.

15 For reasons which are not currently understood, these images suggest that  
sputter depositing silica on the surface of the glass yields a coating with a surface  
having a series of fairly sharp, distinct peaks. No meaningful statistical analysis of  
coated surfaces have been performed, so it is not known if Figures 6-10 are  
20 10 representative of their respective surfaces. As a matter of fact, it is acknowledged that  
these images could be atypical of the overall surfaces of the samples in question, so it  
may not be appropriate to attach too much significance to the apparent differences in  
the surface structure of these two glasses. However, this data does suggest that the  
25 surface of the water-sheeting coating 20 of the invention is relatively non-porous and  
15 differs from an untreated float glass surface in that it is significantly more uneven and  
irregular, having a number of discrete, spaced-apart peaks rising significantly above  
the rest of the surface.  
30

The behavior of a sheet of glass coated with a water-sheeting coating of the  
invention is visibly different from that of a similar sheet of glass not bearing the present  
35 20 coating. A glass surface bearing a water-sheeting coating 20 tends to sheet water  
more readily and is noticeably easier to clean without any visible streaks or defects  
than is a comparable sheet of glass under the same conditions.

40 To provide an accurate comparison of a coating of the invention to a directly  
comparable sheet of glass not bearing the coating, a comparative sample was  
25 prepared. A plain, untreated pane of glass was thoroughly cleaned and laid  
horizontally on a set of rollers. A small, square piece of glass was laid on the upper  
45 surface of the pane of glass to serve as a template covering part of the surface of the  
pane. The pane and overlying template were passed into a magnetron sputtering  
chamber and a coating of about 35 Å of SiO<sub>2</sub> was deposited. The template was then  
50 30 removed, leaving a pane of glass with a water-sheeting coating 20 of the invention  
over most of its surface, but having an uncoated area which was beneath the template

5 during the sputtering operation. The opposite side of the glass, i.e., the side of the  
glass facing away from the side provided with the SiO<sub>2</sub> coating, was coated with a low  
10 emissivity, Infrared-reflective film stack having two silver layers spaced apart from one  
another and from the glass using a plurality of dielectric layers.

5 The partially coated surface of the glass pane was visibly inspected. When  
completely clean, the boundaries of the uncoated area which underlied the template  
15 during sputtering was essentially undetectable to the unaided eye, indicating that the  
water-sheeting coating had a minimal impact on the basic optical properties of the  
glass. A fine spray of atomized water droplets was sprayed on the surface using a  
20 10 simple, hand-operated spray bottle of the type conventionally used to spray household  
cleaning products. Once the spray was applied, the boundaries of the uncoated area  
were readily visible. The water on the area bearing the coating 20 sheeted to an  
apparently uniform film of water, but the area without the coating had a less uniform  
25 appearance.

15 A conventional cleaning solution commercially available under the trademark  
Windex® was sprayed on the surface of the glass pane and the surface was wiped with  
30 a paper towel until the area bearing the coating 20 appeared dry and no longer  
showed any visible streaks. When wiping ceased, the uncoated area still had visible  
streaks of moisture. While these visible streaks on the uncoated area eventually dried  
35 20 without leaving any substantial residual streaking on the glass, it is believed that the  
average person would tend to continue to wipe this area until all visible streaks  
disappeared, meaning that the person would expend less time and effort cleaning a  
glass article bearing a water-sheeting coating 20 than a glass article without such a  
40 coating.

25 The change in surface properties brought about by the present invention are  
readily discernable on a qualitative level, but it can be more difficult to quantify these  
45 differences in a meaningful manner. Nonetheless, the following examples are  
believed to illustrate the difference between an uncoated sheet of glass and a sheet of  
glass bearing a water-sheeting coating 20 of the invention. In each of the following  
50 30 Experimental Examples 1-3, two test samples, Sample A and Sample B, were  
provided. Sample A comprised a plain sheet of soda-lime glass and Sample B was a

similar sheet of soda-lime glass bearing a water-sheeting coating 20 of the invention. The water sheeting coating was applied using three 95% silicon/5% aluminum rotary targets at a power level of 42 kW in an oxygen atmosphere of about 3.5 mT with the glass moving at a rate of about 500 inches per minute.

#### 5 EXPERIMENTAL EXAMPLE 1

Both of the samples were subjected to a salt spray test in accordance with ASTM B117 using a 5% salt solution for 250 hours. Briefly, the samples were cleaned and placed in a Singleton SCCH #20 Corrosion Cabinet at an angle of about 15-30° from vertical, with Sample B being oriented such that the surface bearing the water-sheeting coating 20 was oriented to face downwardly. A 5% salt solution (5 wt% sodium chloride, 95 wt% distilled water) was atomized in the cabinet at about 35° C for 250 hours, with the salt solution being collected at a rate of about 1.8 ml per 80 cm per hour in the collection cylinders in the cabinet. Thereafter, the samples were removed from the cabinet, rinsed, allowed to dry and visually inspected. Sample A had more numerous water spots than did Sample B and the water spots on Sample A were more visible than the light streaks on Sample B.

Each sample was then cleaned using paper towels and Windex®. The haze of each sample was then measured using a BVK-Gardner Haze-Gard Plus according to ASTM D-1003 and ASTM D-1044, employing an integrating sphere integrating light over the spectral range associated with the CIE-C standard. Sample A, the standard glass sheet, had a haze measurement of about 0.15% while the haze measurement on Sample B, the sample bearing a water-sheeting coating 20, was about 0.10%.

The contact angle of the water on the surface of the glass sheet was then measured using a commercially available measuring device, with the contact angle for Sample B being measured on the surface bearing the coating 20. The contact angle for Sample A was about 32 degrees; the contact angle for Sample B was about 12 degrees.

#### 50 EXPERIMENTAL EXAMPLE 2

5 Handling the samples with tongs, each sample was first dipped in a beaker of  
boiling tap water maintained at about 100° C and held there for about 5 seconds, after  
10 which it was deposited in a beaker of ice water maintained at about 0° C and held  
there for about 5 seconds. This process was repeated 25 times. The samples were  
15 then placed in a Singleton Model SL23 humidity test chamber maintained at about  
90% relative humidity at about 120° F (about 49°C) for about 500 hours. Each sample  
was then visually inspected. As in Experimental Example 1, it was determined that  
20 Sample A exhibited more numerous and more visible water spots than did Sample B.

Each sample was then cleaned and the haze and contact angle measurements  
10 were taken in much the same manner outlined above in Experimental Example 1. The  
haze measurement for Sample A was 0.34% while that for Sample B was 0.14%.  
25 Sample A exhibited a contact angle of about 20° while the contact angle for Sample B  
was about 12°.

### 30 EXPERIMENTAL EXAMPLE 3

15 Two samples of uncoated glass (Samples A1 and A2) and two samples of  
coated glass (Samples B1 and B2) were cleaned and their haze measurements were  
35 taken. Each of the uncoated samples had haze measurements of about 0.09% while  
the haze measurement for the glass with a water-sheeting coating 20 was about  
0.08%.

40 20 A cement mixture was prepared by mixing 4 ounces (about 11.5 g) of portland  
cement to 1000 ml of water. Two samples of uncoated glass (Samples A1 and A2)  
and two samples of coated glass (Samples B1 and B2) were held in this solution for  
45 about ten minutes then removed. Samples A1 and B1 were then rinsed liberally with  
water (but without any rubbing) and allowed to dry; Samples A2 and B2 were allowed  
25 to air dry without rinsing.

50 All four samples were hand cleaned using Windex® and paper towels. The  
residual soiling on Samples A1 and A2 from the cement test smeared during this

cleaning, making it more difficult to clean the glass. In contrast, neither Samples B1  
not Sample B2 smeared and both of these samples dried noticeably quicker than  
Sample A1 or Sample A2, respectively.

Once the samples had been thoroughly hand cleaned, haze and contact angle  
measurements were made. After the cement treatment, the haze for Samples A1 and  
B1 remained unchanged at 0.09% and 0.08%, respectively. The haze measurement  
for Sample B2 likewise remained unchanged at about 0.08%, but the haze  
measurement for Sample A2 increased slightly from about 0.09% to about 0.10%.  
The contact angle for Samples A1 and A2 were measured prior to the cement  
treatment at about 26°; Samples B1 and B2 had contact angles of about 11° at the  
same stage. After the cement treatment, the contact angle for Sample A1 was about  
32° while the contact angle for Sample B1, the other rinsed sample, was about 10°.  
The contact angle for Sample A2 was about 33° while the contact angle for Sample  
B2, the other air-dried sample, was about 14°.

#### EXPERIMENTAL EXAMPLE 4

The performance of glass bearing a water-sheeting coating of the invention  
was compared to plain, uncoated glass and to other glass coatings which claim to  
make the surface easier to clean. Each sample started with a sheet of float glass and,  
aside from the uncoated glass sample, had a coating applied to a surface thereof; the  
sample ID assigned to each sample type and the coating applied thereto is set forth in  
the following table:

Sample ID	Coating applied
168	35Å SiO <sub>2</sub> sputtered using 100% O <sub>2</sub>
169	50Å SiO <sub>2</sub> sputtered using 100% O <sub>2</sub>
170	50Å SiO <sub>2</sub> sputtered using 80/20 mixture of O <sub>2</sub> /Ar
171	100Å SiO <sub>2</sub> sputtered using 80/20 mixture of O <sub>2</sub> /Ar
173	Window Maid™ coating, commercially available from _____, applied in accordance with manufacturer's instructions
174	Glass Shield™ coating, commercially available from _____, applied in accordance with manufacturer's instructions
175	Clear Shield™ coating, commercially available from _____, applied in accordance with manufacturer's instructions
176	uncoated glass

- 29 -

A set of these samples were subjected to an accelerated weathering test and the contact angle and ease of cleaning was checked on a periodic basis. In the weathering test, the samples were placed in a stainless steel enclosure maintained at a temperature of about 160°F (about 71°C). A 300W ultraviolet light source (sold by Osram under the trade name Ultra-Vitalux) was positioned toward the bottom of the enclosure and samples were positioned at an angle of about 45° with respect to horizontal with the bottom edges of the sample spaced about 10 inches (about 25 cm) from the bulb. Periodically, the samples were removed from the enclosure and the contact angle was measured in much the same manner as that outlined above. The contact angles were as follows:

Sample ID	Contact Angle, by number of days in weathering test						
	0	1	2	3	4	5	10
168	13			20			
169	11	14.3	17.7	21	27	33	
170	11			17	25.5	34	
171	6	26.5	26.5	32	33	34	
173	41			50	51.5	53	42
174	23			48	48.5	49	46
175	74			62	66	70	66
176	35	35				31	35

In addition, the ease of cleaning the sample was tested by spraying Windex® on the coated surface of the sample or, in the case of the uncoated sample, on the surface which was in contact with the tin bath during the float manufacturing process. That surface was manually wiped with a paper towel until the surface appeared to be clean and essentially streak-free. The ease of cleaning was determined on scale of 1-5, with the ease of cleaning normal, uncoated glass prior to any environmental exposure being defined as 3, a very easy to clean glass surface being rated 1 and a sample which is substantially more difficult to clean being rated 5. (While this rating system is somewhat subjective, it does give a rough qualitative indication of the ease with which the glass can be cleaned.) The results of this testing were as follows:

Sample ID	Contact Angle, by number of days in weathering test						
	0	1	2	3	4	5	10
168	1	1.5	1.5	2	3		
169	1	1.5	1.5	2	3	4	



170	1	1	1	1.5	3	4	
171	1	3	3	3	3	4	
173	4	4	4	5	5	4	4
174	5	5	5	5	5	5	5
175	5	5	5	5	5	5	5
176	3	3					3

These results indicate that a water-sheeting coating 20 of the invention makes the glass surface significantly easier to clean than either the standard, uncoated glass or glass coated with any one of several commercially available coatings designed to make glass easier to clean. As a matter of fact, these commercially available coatings actually made the glass seem more difficult to clean. (While these coatings may be effective in some applications, it is believed that the "ease of cleaning" standards employed in this Experimental Example are fairly representative of how an average home owner would perceive ease of cleaning. For example, even if streaks of the cleaning fluid on the pane of glass might dry without leaving any permanent streaks, an average person is likely to keep wiping the area until the glass appears clean to avoid any residual streaking.)

The advantageous effects of the water-sheeting coating of the invention did appear to drop off over time in this accelerated weathering test. In particular, after 5 days or so in this test, coatings of the invention yielded results comparable to those achieved with uncoated glass samples. Even after such degradation, the samples bearing a water-sheeting coating 20 had a lower contact angle and remained easier to clean than did the commercially available coatings evaluated in these tests.

It is unclear what correlation there may be between time of ordinary exposure to the elements and time in the accelerated weathering test used in this example. It is believed, however, that a coating 20 of the invention will continue to show enhanced cleanability for an extended period of time. As a matter of fact, preliminary tests indicate that much of the benefit of the coating 20 may be restored with appropriate cleaning even after degradation in accelerated weathering testing, suggesting that the benefits of the coating can be restored relatively simply even after they have diminished due to exposure to the elements.

5

10

15

20

25

30

35

40

45

50

55

While a preferred embodiment of the present invention has been described, it should be understood that various changes, adaptations and modifications may be made therein without departing from the spirit of the invention and the scope of the appended claims.

**Claims**

5

10

15

20

25

30

35

40

45

50

55

## WHAT IS CLAIMED IS:

1. A sheet of glass having an interior surface bearing a reflective coating thereon and an exterior surface bearing a water-sheeting coating thereon, the reflective coating comprising a reflective metal layer and at least one dielectric layer, the water-sheeting coating comprising silica sputtered directly onto the exterior surface of the sheet of glass, the water-sheeting coating having an exterior face which is substantially non-porous but which has an irregular surface, the water-sheeting coating reducing the contact angle of water on the coated exterior surface of the glass article below about 25° and causing water applied to the coated exterior surface of the pane to sheet.
2. The invention of claim 1 wherein the reflective coating is an infrared reflective coating comprising, in sequence moving outwardly from the interior surface of the sheet of glass, said at least one dielectric layer, the reflective metal layer and a second dielectric layer, the infrared reflective coating having a transmittance of at least about 70% in the visible spectrum.
3. The invention of claim 1 further comprising a spacer and a second sheet of glass having an interior surface, the spacer being disposed between the interior surfaces of the sheets of glass and serving to maintain those interior surfaces in a spaced-apart parallel relationship and defining an interpane space therebetween.
4. The invention of claim 1 further comprising a tear-resistant plastic film and a second sheet of glass having an interior surface, the resilient plastic film being bonded on one side to the interior surface of one of the sheets of glass and on

its other side to the interior surface of the other sheet of glass, thereby forming a laminate structure.

5. A method of rendering a surface of a pane of glass resistant to soiling and staining, comprising:

providing a sheet of glass having a clean interior surface and a clean exterior surface;

coating the interior surface of the sheet of glass with a reflective coating by sputtering, in sequence, at least one first dielectric layer, at least one metal layer, and at least one second dielectric layer;

coating the exterior surface of the glass with a water-sheeting coating by sputtering silica directly onto the exterior surface of the sheet of glass.

6. The method of claim 5 wherein the layer of silica is sputtered onto the exterior surface of the glass by sputtering a silicon target in an oxygen-containing sputtering chamber.

7. The method of claim 5 wherein the sheet of glass is passed through a series of sputtering chambers retaining a corresponding series of sputtering targets spaced outwardly from the interior surface of the sheet of glass, the first dielectric layer being applied in a first of the sputtering chambers, the metal layer being applied in a second of the sputtering chambers and the second dielectric layer being applied in a third of the sputtering chambers.

8. The method of claim 7 wherein one of the first and third sputtering chambers includes a silicon-containing target spaced outwardly from the exterior surface of the sheet of glass, the water-sheeting coating being applied by sputtering the

5

silicon-containing target in the same sputtering chamber in which one of the dielectric layers is applied.

10

9. The method of claim 8 wherein the sputtering chamber within which the silicon-containing target is retained is provided with an oxidizing sputtering atmosphere.

15

10. A method of rendering a surface of a pane of glass resistant to soiling and staining, comprising:

20

providing a sheet of glass having a clean interior surface and a clean exterior surface and a sputtering line comprising a series of sputtering chambers each having a support for a sheet of glass therein, at least one of the sputtering chambers comprising a downward sputtering chamber having an upper target positioned above the support, a second of the sputtering chambers comprising an upward sputtering chamber having a lower target positioned below the support;

15

positioning the sheet of glass on the support in the downward sputtering chamber such that the interior surface is oriented toward the upper target and sputtering the upper target to deposit a dielectric layer on one of the interior surface of the glass or a film stack layer previously deposited on the interior surface of the glass;

35

40

20

positioning the sheet of glass on the support in the upward sputtering chamber such that the exterior surface is oriented toward the lower target and sputtering the lower target to deposit a water-sheeting coating on the exterior surface of the glass.

45

50

55

- 5
11. The method of claim 10 wherein the upward sputtering chamber further  
comprises an upper target positioned above the support, further comprising  
10 sputtering the upper target to deposit a dielectric layer on one of the interior  
surface of the glass or a film stack layer previously deposited on the interior  
15 surface of the glass while the sheet of glass remains in the upward sputtering  
chamber.
12. A method of rendering a surface of a pane of glass resistant to soiling and  
20 staining, comprising:  
providing a sheet of glass having a clean interior surface and a clean exterior  
10 surface and a sputtering line comprising a series of sputtering chambers  
each having a support for a sheet of glass therein, at least one of the  
25 sputtering chambers comprising a dual direction sputtering chamber  
having an upper target positioned above the support and a lower target  
30 positioned below the support;  
15 positioning the sheet of glass on the support in the dual direction sputtering  
35 chamber such that the interior surface is oriented toward the upper target  
and the exterior surface is oriented toward the lower target; and  
40 while the sheet of glass remains in the dual direction sputtering chamber
- 45
- 50
- 55

- 36 -

i) sputtering the upper target to deposit a dielectric layer on one of the interior surface of the glass or a film stack layer previously deposited on the interior surface of the glass; and

ii) sputtering the lower target to deposit a water-sheeting coating on the exterior surface of the glass.

13. A method of coating two sides of a single pane of glass in a single pass through a coating apparatus, comprising:

providing a sheet of glass having a clean interior surface and a clean exterior surface and a sputtering line comprising a series of sputtering chambers each having a support for a sheet of glass therein, at least one of the sputtering chambers comprising a downward sputtering chamber having an upper target positioned above the support, a second of the sputtering chambers comprising an upward sputtering chamber having a lower target positioned below the support;

positioning the sheet of glass on the support in the downward sputtering chamber such that the interior surface is oriented toward the upper target and sputtering the upper target to deposit a coating directly on one of the interior surface of the glass or a film stack layer previously deposited on the interior surface of the glass;

positioning the sheet of glass on the support in the upward sputtering chamber such that the exterior surface is oriented toward the lower target and sputtering the lower target to deposit a coating on one of the exterior



- 37 -

5

surface of the glass or a film stack layer previously deposited on the  
exterior surface of the glass,

10

the glass being coated on both the interior surface and the exterior surface  
while maintaining a constant orientation wherein the interior surface is

15

positioned above the exterior surface.

14. The method of claim 13 wherein the lower target comprises silicon, said lower  
target being sputtered in an oxidizing atmosphere to deposit a water-sheeting  
coating directly on the exterior surface of the glass.

20

25

30

35

40

45

50

55

1/10

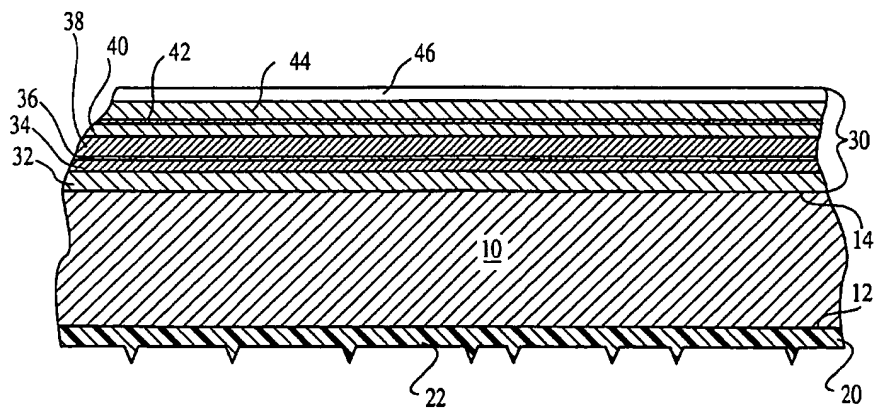


FIG. 1

2/10

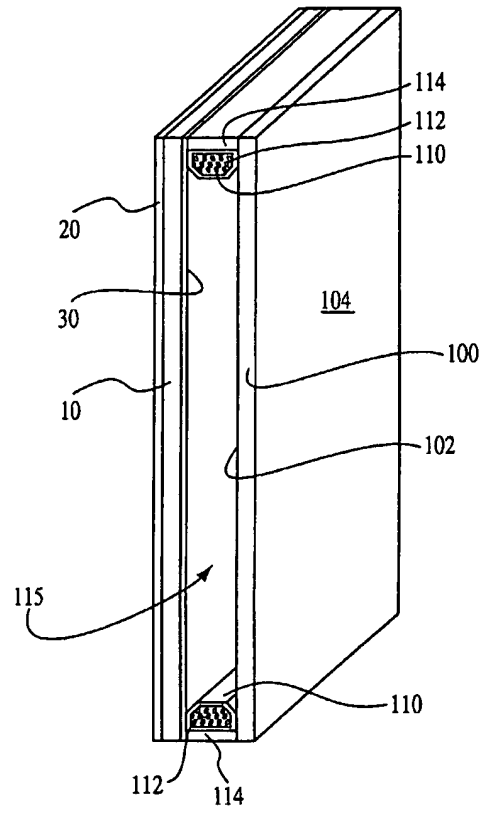


FIG. 2

3/10

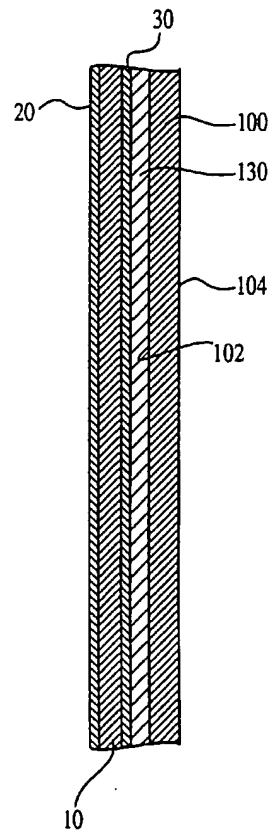


FIG. 3

4/10

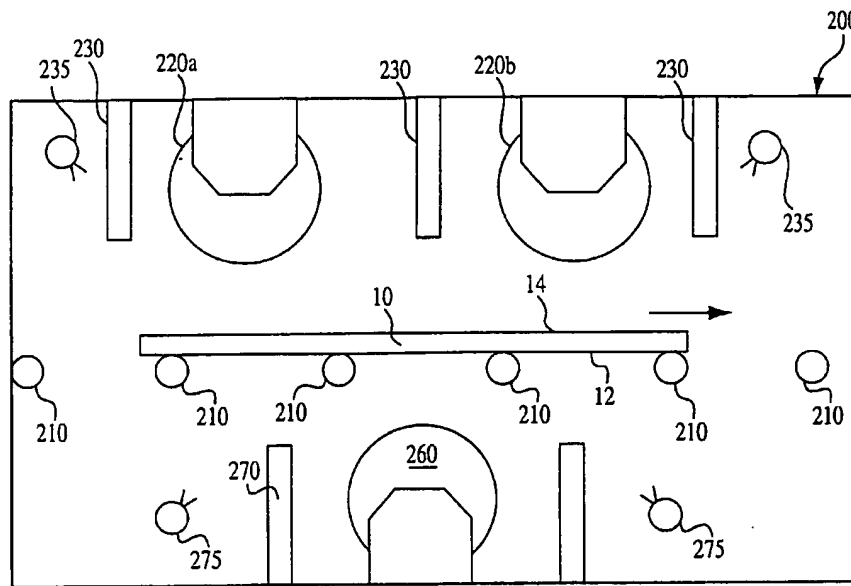


FIG. 4

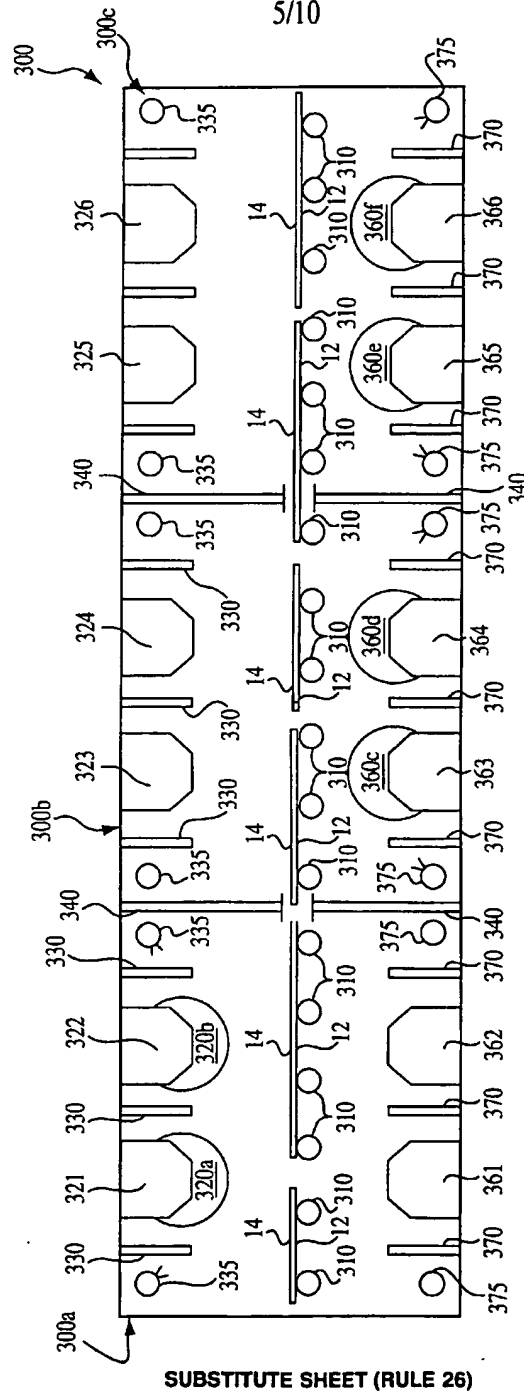


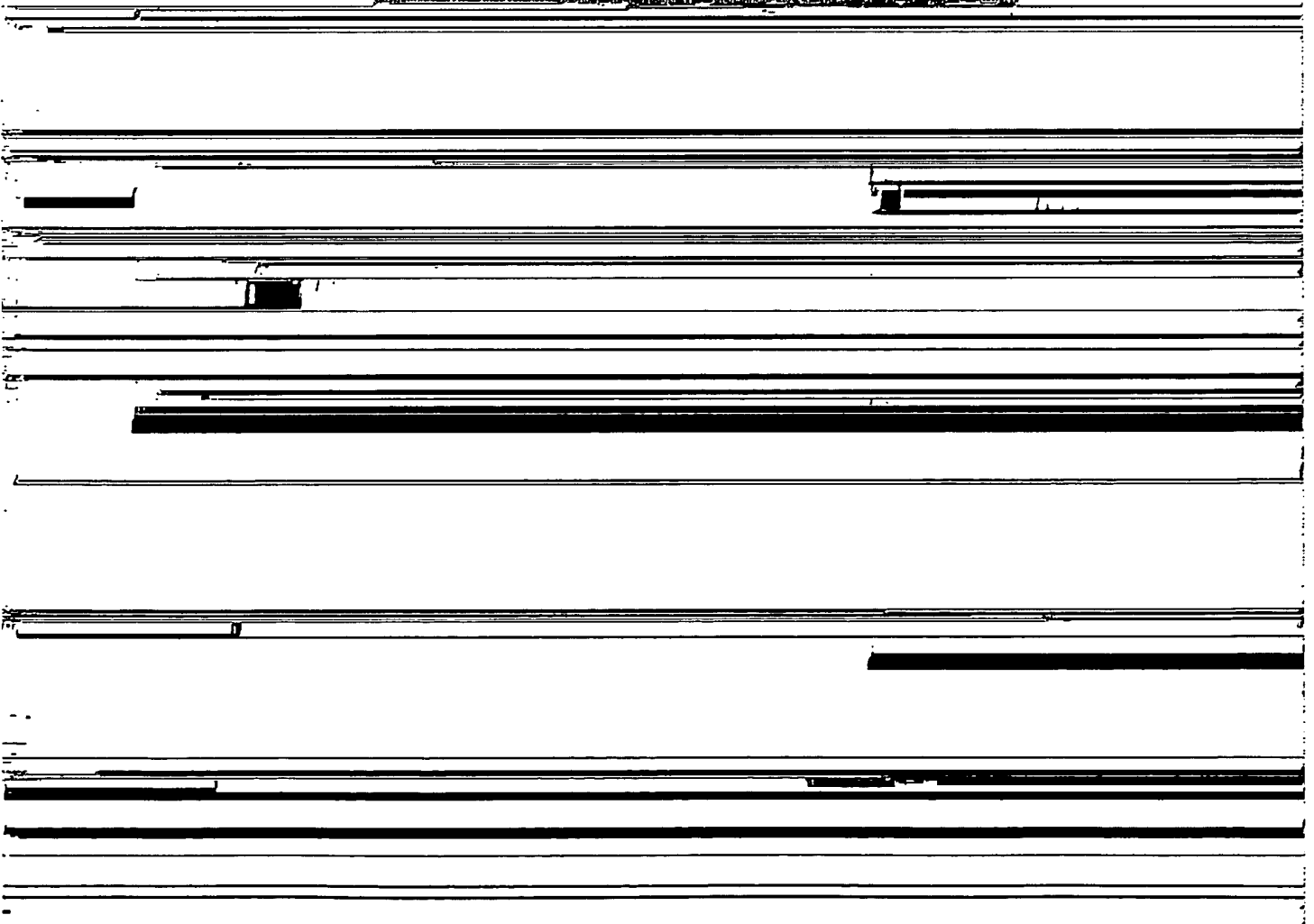
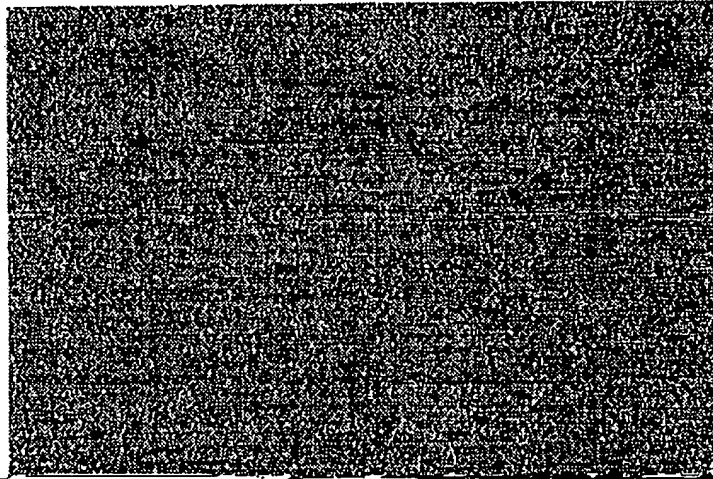
FIG. 5

# BEST AVAILABLE COPY

WO.00/37377

PCT/US99/02208

6/10



7/10

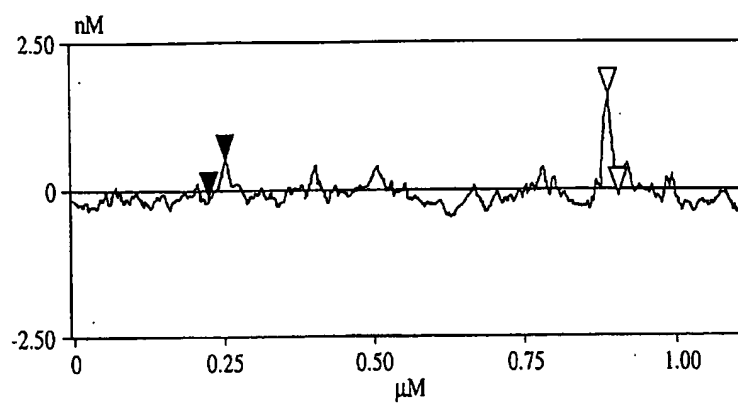


FIG. 7

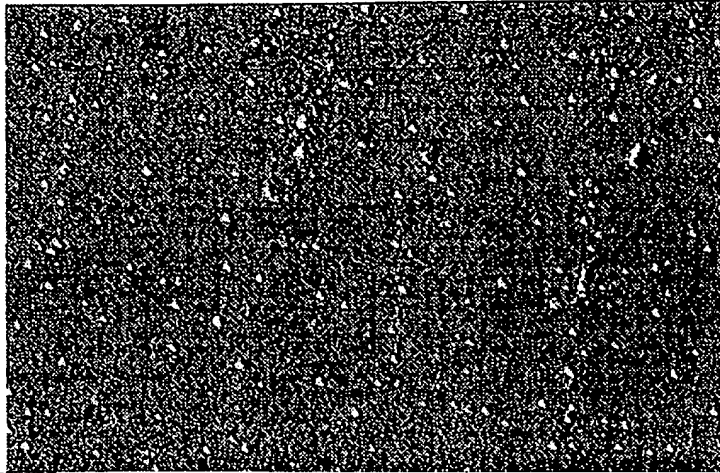


# BEST AVAILABLE COPY

WO-00/37377

PCT/US99/02208

8/10



# BEST AVAILABLE COPY

WO.00/37377

PCT/US99/02208

9/10

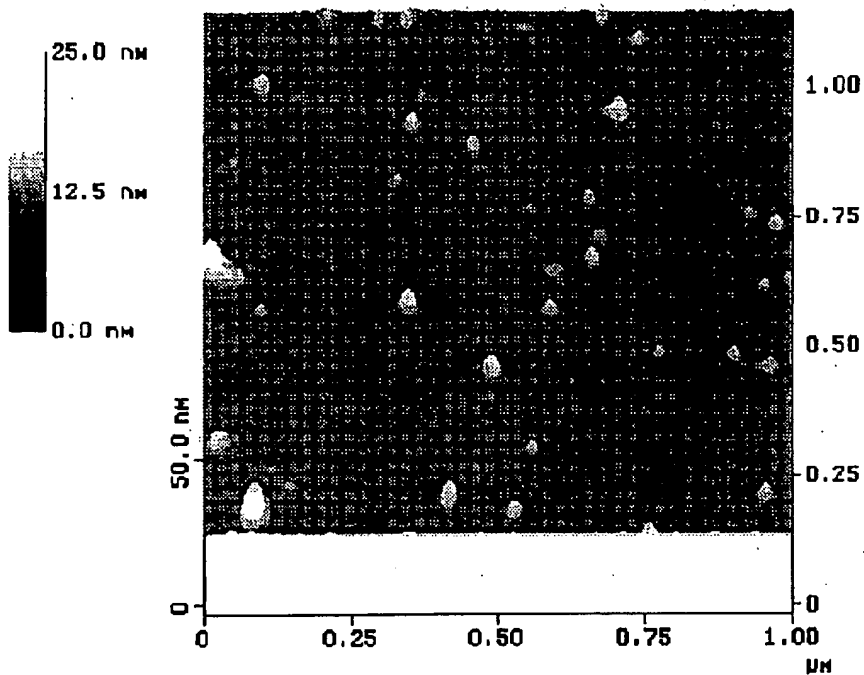


FIG. 9

SUBSTITUTE SHEET (RULE 26)

10/10

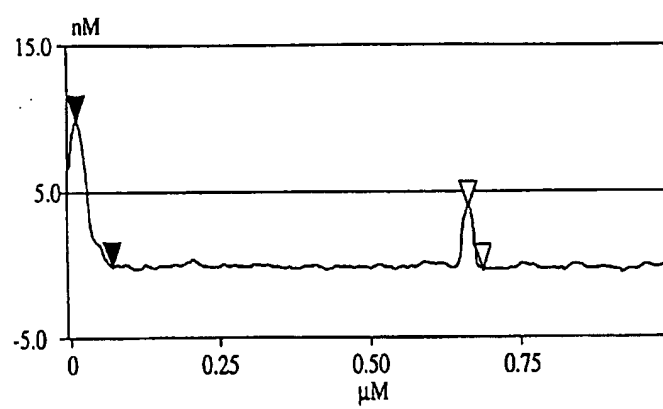


FIG. 10

# INTERNATIONAL SEARCH REPORT

Int. Application No.  
PCT/US 99/02208

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C03C17/34 C03C17/36 C23C14/56

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C03C C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 689 962 A (MURAKAMI KAIMEIDO KK) 3 January 1996 (1996-01-03) the whole document ---	1-12
A	EP 0 820 967 A (MURAKAMI CORP) 28 January 1998 (1998-01-28) claims ---	1-12
A	EP 0 637 572 A (CARADON EVEREST LTD) 8 February 1995 (1995-02-08) the whole document ---	1-12
A	US 5 733 660 A (TAKAMATSU ATSUSHI ET AL) 31 March 1998 (1998-03-31) abstract --- -/-	1-12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

17 November 1999

Date of mailing of the international search report

29.11.99

Name and mailing address of the ISA

European Patent Office, P.B. 5618 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl  
Fax: (+31-70) 340-3016

Authorized officer

Van Bommel, L

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/02208

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 762 674 A (WETMORE KENNETH H ET AL) 9 June 1998 (1998-06-09) abstract; figures	1-14
A	US 5 211 759 A (ZIMMERMANN HEINRICH ET AL) 18 May 1993 (1993-05-18) abstract; figures	1-14
X	WO 92 17621 A (CONNER PERIPHERALS INC) 15 October 1992 (1992-10-15) page 21, line 9 - line 14 page 28, line 2 - line 6 abstract; figure 1	13
A		14
A	DE 43 13 284 A (LEYBOLD AG) 27 October 1994 (1994-10-27) column 2, line 25 -column 3, line 57; figure	13,14

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 99/02208

## Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(e).

## Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 99/02208

FURTHER INFORMATION CONTINUED FROM PCT/8A/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-12

Sheet of glass with a reflecting coating on one surface and a water-sheeting coating on the other surface; methods for rendering a surface of a glass sheet resistant to soiling and staining by sputter coating a water-sheeting layer on one side of the glass sheet and a reflecting and/or dielectric layer on the other side.

2. Claims: 13-14

Method of sputter coating two sides of a glass pane in a single pass through a sputtering apparatus, regardless of the nature of the coating.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/02208

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0689962 A	03-01-1996	JP 8011631 A US 5594585 A	16-01-1996 14-01-1997
EP 0820967 A	28-01-1998	JP 2901550 B JP 10036144 A US 5854708 A	07-06-1999 10-02-1998 29-12-1998
EP 0637572 A	08-02-1995	GB 2280699 A	08-02-1995
US 5733660 A	31-03-1998	JP 2895749 B JP 7315882 A JP 2895746 B JP 7315879 A	24-05-1999 05-12-1995 24-05-1999 05-12-1995
US 5762674 A	09-06-1998	AU 6917596 A EP 0852570 A WO 9711916 A US 5876474 A	17-04-1997 15-07-1998 03-04-1997 02-03-1999
US 5211759 A	18-05-1993	DE 59202577 D EP 0502385 A	27-07-1995 09-09-1992
WO 9217621 A	15-10-1992	EP 0577766 A JP 6510565 T US 5814196 A US 5683561 A	12-01-1994 24-11-1994 29-09-1998 04-11-1997
DE 4313284 A	27-10-1994	NONE	